"Gas-producing mixtures"

Gas generators are being used to an increasing extent, for example in motor vehicles for life-saving purposes. The gas-producing mixture usually contains sodium azide. Sodium azide as such is poisonous, and it can readily react with heavy metals, e.g. copper and lead, to form extremely dangerous and vigorously reacting compounds. Special precautions must therefore be taken in the production of the raw material and of the gas charge mixture, in its processing and in quality control. For this reason the disposal of the sodium azide, for example when exchanging defective gas generators or when scrapping vehicles, also presents a particular problem. Improper use must also be reliably prevented.

There has been no lack of attempts to use other substances in place of sodium azide. A common feature of all proposed replacements for sodium azide is that they contain organic carbon compounds, and as a rule also organic nitrogen compounds. EP 0 519 485 describes the use of tetrazole or a derivative or derivatives of tetrazole, or the use of one or more compounds from the group consisting of cyanic acid derivatives and their salts, one or more compounds from the group consisting of triazine and triazine derivatives, the use of urea, its salts, derivatives and salts of these compounds: these compounds can also be present as mixtures. Ammonium nitrate and nitrates of sodium, potassium, magnesium, calcium and iron, and/or peroxides of zinc, calcium, strontium or magnesium, can be used as oxidants. Other gas-producing components, cooling agents, reducing agents, catalysts and/or porosity producing agents can be added.

EP 0 438 851 describes a non-toxic, non-azide

pyrotechnic composition which is suitable for use in the production of substantially non-toxic combustion products that include a gas in order to fill an accident cushion. The composition includes a mixture of at least one tetrazole or tetrazole compound containing hydrogen in its molecule, at least one oxygen-containing oxidant and at least one metal oxide selected from cobalt oxide, nickel oxide, chromium oxide, aluminium oxide and boron oxide. In the combustion a substantially non-toxic primary gas mixture and filterable solids are produced. Aminotetrazole, together with oxidants which can contain perchlorates as well as nitrates, is employed, by way of example.

A similar formulation is disclosed in European patent EP 0 372 733: the use of tetrazoles and triazoles in mixtures with ammonium perchlorate and alkali nitrate as oxidants, in combination with an additive to control combustion.

PCT application WO 94/01381 describes a gas-producing agent for airbags consisting of organic nitrocompounds and halogenates. By halogenates are to be understood, for example, alkali metal chlorates, bromates and their per-compounds. The following are mentioned, inter alia, as combustion-controlling catalysts: oxides, chlorides, carbonates, sulphonates of the 4th to 6th series of the periodic classification.

When the above-mentioned gas charges undergo reaction to inflate airbags for motor vehicle safety, proportions of toxic gases such as, for example, carbon monoxide or nitrogen oxides can be present besides non-toxic working gases such as nitrogen, carbon dioxide and hydrogen. Limits such as, for example, the maximum allowable concentration (MAC) in the workplace, are set having regard to peak loads for these gases. Their

formation is thermodynamically and kinetically connected, and in the case of carbon monoxide is controlled e.g. by the producer gas equilibrium. It has further been found that mixtures which contain nitrogen- and carbon-containing compounds and evolve small proportions of NO_x during combustion evolve large proportions of CO, and vice versa. The establishment of these equilibria is temperature and pressure-dependent. It is known that a sufficiently effective influencing of the composition of the reaction gases towards the formation of non-toxic products cannot be achieved solely by physical measures, for example control of the reaction by pressure and/or temperature.

Processes are known from the literature which have the object of reducing these components of the reaction gases. Thus, for example, the equilibrium can be displaced at the expense of carbon monoxide formation by the formation of carbonates by the addition of alkaline slag-forming agents to the gas charge. At the same time nitrogen oxides are converted into nitrates or nitrites.

However, these measures have the disadvantage that the yield of gas is made substantially worse by the high proportion of slag. In addition, the slag must be separated at some expense from the gaseous constituents by filters or other retaining systems before the working gases can be used, for example for the inflation of the airbag.

While the use of nitrogen-free systems does lead to the formation of nitrogen-free gases, this is at the expense of a lower yield of gas. The reason for this is that, to displace the producer gas equilibrium in the direction of CO_2, an excess of slag-forming oxygen-carrying agent must be used. Hence hybrid systems have already been proposed in which the reactions described above are brought about by compressed air instead of by

slag-forming oxidants. However, these concepts suffer from the disadvantage of the high weight of the system and the need to control or supplement the compressed air.

According to US patent 3 910 595, to improve the yield the gas forming in the reaction is passed through a venturi nozzle so that ambient air can be drawn in to assist in the inflation of the airbag. Here, however, it must be taken into account that this ambient air greatly cools the hot gases. Particularly at low ambient temperatures the resulting loss in volume for inflating the gasbag must be compensated for by the pyrotechnic mixture. The resulting increased proportion of toxic reaction gases in the interior of the vehicle can no longer be sufficiently reduced by dilution.

The present invention provides non-toxic, azide-free mixtures for the production of gas by combustion. These gas-producing mixtures can be used, inter alia, in safety devices, for example in airbag systems for inflation of airbags in motor vehicles and aircraft. However, they are also suitable for lifting heavy loads by inflation of bags placed under them, or for expulsion of e.g. fire extinguishing powder, or for other measures where the performance of work requires rapid formation of gases.

The mixtures in accordance with the invention contain:

a) as nitrogen-containing compound (fuel) at least one compound from the group: tetrazole, triazole, triazine, cyanic acid, urea, their derivatives or their salts;

b) as oxidant, at least three compounds from the group of the peroxides, nitrates, chlorates or perchlorates;

c) combustion moderators which are capable of

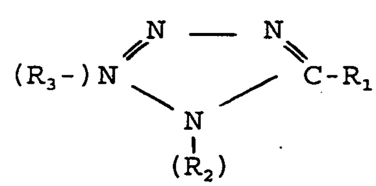
influencing the combustion and its rate by heterogeneous or homogeneous catalysis; and optionally also

d) additions which are capable of reducing the proportion of the toxic gases.

The mixtures in accordance with the invention are not toxic, and in contrast to azide-containing mixtures are easy to handle. They therefore require less outlay on safety in the production of the raw materials and mixtures and in their shaping, storage or disposal.

The nitrogen-containing compounds to be used according to the invention are those which, in the mixture with oxidants, mainly form in their thermal/chemical reaction CO_2, N_2, O_2 and H_2O, but do not evolve any gases such as CO or NO_x in concentrations that could endanger health.

The mixtures according to the invention preferably contain as nitrogen-containing compounds (fuels) one or more tetrazole derivatives of the formula:



in which R_1 and R_2 or R_3 can be the same or different, with either R_2 or R_3 being present, and standing for hydrogen, hydroxy, amino, carboxyl, an alkyl radical with 1 to 7 carbon atoms, an alkenyl radical with 2 to 7 carbon atoms, an alkylamino radical with 1 to 10 carbon atoms, an aryl radical, optionally substituted with one or more substituents which can be the same or different and are selected from the amino group, the nitro group, alkyl radicals with 1 to 4 carbon atoms or an arylamino radical in which the aryl radical can optionally be substituted, or the sodium, potassium and

guanidinium salts of the said tetrazole derivatives.

In these compounds:

R_1 preferably stands for hydrogen, amino, hydroxy, carboxyl, a methyl, ethyl, propyl or isopropyl, butyl, isobutyl or tert-butyl, n-pentyl, n-hexyl, or n-heptyl radical, a methylamino, ethylamino, dimethylamino, n-heptylamino, n-octylamino or n-decylamino radical, a tetrazole radical, a phenylamino radical, a phenyl, nitrophenyl or aminophenyl radical; and

R_2 or R_3 preferably stands for hydrogen, a methyl or ethyl radical, a phenyl, nitrophenyl or aminophenyl radical.

Particularly preferred compounds are the tetrazole derivatives 5-aminotetrazole, lithium, sodium, potassium, zinc, magnesium, strontium or calcium 5-aminotetrazolate, 5-aminotetrazole nitrate, sulphate, perchlorate and similar compounds, 1-(4-aminophenyl)-tetrazole, 1-(4-nitrophenyl)-tetrazole, 1-methyl-5-dimethylaminotetrazole, 1-methyl-5-methylamino tetrazole, 1-methyltetrazole, 1-phenyl-5-aminotetrazole, 1-phenyl-5-hydroxytetrazole, 1-phenyltetrazole, 2-ethyl-5-aminotetrazole, 2-methyl-5-aminotetrazole, 2-methyl-5-carboxytetrazole, 2-methyl-5-methylaminotetrazole, 2-methyltetrazole, 2-phenyltetrazole, 5-(p-tolyl)tetrazole, 5-diallylamino tetrazole, 5-dimethylaminotetrazole, 5-ethylamino tetrazole, 5-hydroxytetrazole, 5-methyltetrazole, 5-methylaminotetrazole, 5-n-decylaminotetrazole, 5-n-heptylaminotetrazole, 5-n-octylaminotetrazole, 5-phenyltetrazole, 5-phenylaminotetrazole or bis-(aminoganidine)-azotetrazole and diguanidinium-5,5'-azotetrazolate, as well as 5,5'-bitetrazole and its salts, such as the 5,5'-bi-1H-tetrazole ammonium compounds.

The mixtures may contain: as triazine derivatives, 1,3,5-triazine, as triazole derivatives, 1,2,4-

triazole-5-one, 3-nitro-1,2,4-triazole-5-one, as cyanic acid derivatives, sodium cyanate, cyanuric acid, cyanuric acid esters, cyanuric acid amide (melamine), 1-cyanoguanidine, sodium dicyanamide, disodium cyanamide, dicyanodiamidine nitrate, dicyanodiamidine sulphate, and as urea derivatives biuret, guanidine, nitroguanidine, guanidine nitrate, aminoguanidine, aminoguanidine nitrate, thiourea; triaminoguanidine nitrate, aminoguanidine hydrogen carbonate, azodicarbonamide, tetracene, semicarbazide nitrate, as well as urethanes, ureides such as barbituric acid, and derivatives thereof.

5-aminotetrazole is used as a particularly preferred component. When this component is used in the mixture the preferred proportion is 10-40% by wt. As derivatives of 5-aminotetrazole, its salts in which the acidic hydrogen atoms in 5-aminotetrazole are replaced in salt-like manner by toxicologically acceptable elements such as calcium, magnesium or zinc, are used. However, compounds in which the cation is ammonium, guanidinium and its amino derivatives can also be used.

Oxidants which may be used according to the invention are:

- peroxides of alkali and alkaline earth metals, zinc peroxide, and the peroxodisulphates of the said elements and ammonium peroxodisulphate;
- ammonium nitrate, nitrates of alkali and alkaline earth metals, in particular lithium, sodium or potassium nitrate, and strontium nitrate;
- halogen oxycompounds of the alkali or alkaline earth metals or of ammonium, particularly preferably potassium perchlorate or ammonium perchlorate.

The oxidants can be used singly or in mixtures. In order to reduce the proportion of nitrogen oxides in the reaction mixture as far as possible, it is advantageous to keep the proportion of nitrate in the oxidant mixture as small as possible, since part of the nitrate can undergo thermal decomposition.

A preferred combination of the oxidants consists of zinc peroxide, potassium perchlorate and at least one nitrate, preferably sodium nitrate or strontium nitrate, mixed in the ratio 1:2:10 and in a total amount of about 60% by wt. in the gas-producing mixture. The chlorine-containing compounds then react during the combustion to form harmless sodium/potassium chloride. Ammonium perchlorate can also be considered as perchlorate, alone or mixed with another halogen oxycompound, but an excess must be avoided in order to prevent the formation of corrosive hydrochloric acid. If ammonium perchlorate is used, the simultaneous presence of zinc compounds is particularly advantageous, since the risk of hydrochloric acid being formed can thereby be avoided. An excess of sodium and potassium compounds is acceptable, since these compounds react with the reaction gases to form harmless carbonates. The partial or complete replacement of the alkali nitrate by strontium nitrate leads to a marked reduction in the amount of slag.

The ratio of the nitrogen-containing compounds, for example the tetrazoles and triazoles, to the oxidants in the mixture is balanced so that, on combustion of the gas charge mixture, an excess of oxygen is formed. This excess of oxygen displaces the CO/CO_2 equilibrium in the direction of carbon dioxide.

Substances or mixtures thereof which are capable by heterogeneous or homogeneous catalysis of influencing the combustion and its rate are used as combustion moderators. Moderators which intervene in

the reaction through heterogeneous catalysis are metals, metal oxides and/or metal carbonates and/or metal sulphides. Preferred metals to use are boron, silicon, copper, iron, titanium, zinc or molybdenum. Calcium carbonate can also be used. Mixtures of these moderators can likewise be used.

Moderators which intervene in the reaction through homogeneous catalysis are, for example, sulphur, boron, silicon or ferrocene and its derivatives. These moderators are vapourized into the vapour phase as a result of the temperatures occurring in the reaction, and thus can intervene in the reaction either as such or as after-products. The proportion of these substances in the mixture can amount to up to about 8%

Furthermore the mixture according to the invention can contain gas-producing additions which are capable of reducing the proportion of the noxious gases such as nitrogen oxides and/or carbon monoxide. The proportion of these noxious gases in the gas mixture produced is determined by

- the stoichiometric composition of the mixture,
- the temperature and pressure of the reaction,
- additives for influencing the reaction or the after-reaction, and by the
- design of the generator in which the reaction takes place.

While in a closed system, such as, for example, a pressure bomb, it is relatively easy to reach the composition of the gas mixture which approximates to the thermodynamic calculations, this can no longer be achieved under the actual operating conditions in the generator, since during the few milliseconds duration of the reaction the equilibrium cannot be established. According to the invention, therefore, suitable substances which can bring about a catalytic effect are introduced into the mixture or into the region of the

outflowing gases. For this purpose the combustion moderators described above and oxides of precious metals can be used. Further possibilities consist in the use of noble metals such as palladium, ruthenium, rhenium, platinum or rhodium, which employ the excess oxygen in the reaction gases in a subsequent reaction to convert the carbon monoxide. A preferred mode of use contemplates applying the additive materials on ceramic or electrodepositing them on metal grids as a support. Using this method it is possible in particular to reduce the proportion of carbon monoxide in the gas mixture.

To reduce the proportion of NO_x, additional substances are used whose chemical properties catalyse in particular the conversion of nitrogen oxides, for example nitrogen dioxide, to nitrates or nitrites. In principle, all more or less strongly basically reacting substances are suitable.

These include, for example, oxides, hydroxides or carbonates of non-toxic elements such as, for example, those of the alkali and alkaline earth metals, those of zinc, and mixtures of these compounds. When these compounds are used, nitrates and nitrites of the elements are mainly formed. Further suitable materials for reaction with NO_2 are urea, guanidine and its derivatives, compounds having NH_2 groups, such as, for example, amidosulphonic acids, amido complexes and the like, and amides. A particularly preferred embodiment contemplates the use of peroxides in the outlet openings of the generator. A particular advantage of this is that, beside the reduction of the nitrogen oxides by the reaction described above, oxygen is also formed for the following catalytic reaction with carbon monoxide.

The additions according to the invention, either alone or together, can either be introduced directly

into the gas-producing charge or be placed in the outflow passages of the generator. For use in the outlet passages of the generator the additions are suitably used in a compacted form, for example in the form of tablets, pellets or granules. The quantity of the additions used in the charge amounts to about 10% by wt. In the outlet channels the quantity of the additions can be as much as 75% by wt., based on the gas charge.

A reduction in the CO content can surprisingly also be achieved if part of the fuel consists of the salts, particularly the calcium, magnesium or zinc salts, of the aminotetrazole, preferably of the corresponding salts of 5-aminotetrazole, or of urea derivatives. In these cases it suffices to use only two oxidants.

To influence the rate and temperature of reaction further additives can be added. Such additives can for example be boron or metal powders, for example titanium, aluminium, zirconium, iron, copper, molybdenum, as well as their stable hydrides. Their proportion in the additions is of the order of 5 % by wt.

The production of the gas charge mixtures according to the invention is carried out in known manner. For example, the components are mixed dry, sieved, divided into portions and pressed to tablets. The adjustment of the rate of combustion can be achieved through the shape and size of the grains of the bulk material obtained by breaking and sieving out the fragments. The bulk material can be produced in large quantities and adapted to meet particular combustion requirements by mixing fractions with different dynamic liveliness. To improve the safety or improve the results of mixing, premixtures of 2 or 3 components can also be used. A mixture of oxidant and

additions may, for example, be made before it comes into contact with the nitrogen-containing compounds.

However, the mixture can also be produced by kneading water-moistened components, followed by granulating, e.g. by passage through sieves, extrusion or the like. In this case binders, for example waterglass, "inorganic rubber" (phosphorus chloronitrile) or even small proportions of organic binders such as acrylic resin, PTFE, or guar gum, can be used. Since the components employed are neither toxic nor particularly reactive, and can only be caused to react in the enclosed space with the aid of special igniters, no special safety precautions are necessary.

The bulk material thus obtained can be used directly. To avoid abrasion of the loose material in contact with the generators, which would lead to changes in the combustion characteristics and would represent a safety risk through its vigorous combustion, the bulk material can be surface-coated. This can be done through a varnish coating, which can optionally be provided with ignition-promoting additions to assist in the ignition. Ignition-promoting additions that come into consideration are oxidants such as zinc peroxide and metal powders such as titanium and zirconium. The application can be effected by spraying-on the solvent-containing coating agent, e.g. in a drum while evaporating off the solvent.

For special fields of application porous grain structures in the grains can be used. The production of such porous structures can be effected by conventional methods, for example by adding soluble salts and subsequently dissolving them out with suitable solvents or by addition of thermally decomposable substances such as, for example, ammonium bicarbonate, acetone dicarboxylic acid, blowing agents,

peroxides or azo-bisisobutyronitrile, which can then be removed again in a subsequent process step by heating and tempering at elevated temperature. The characteristic is determined by quantity, grain size and distribution. Such gas charges can, for example, be used where gas charges which react in a strongly progressive manner are required.

The ignition of the tailor-made gas charge can be effected by the conventional methods. In doing so it is important that no additional toxic reaction gas components are set free from the igniter after the reaction.

The gas charge mixture is insensitive in respect of its safety characteristics, for example to the effects of abrasion, shock and impact or to ignitability by flame or cerium/iron sparks under normal pressure. In an enclosure, however it burns vigorously when suitably ignited. This provides increased safety in manufacture and handling.

The mixtures according to the invention can, for example, be used in gas generators for motor vehicle safety with the electrically initiated ignition systems conventionally employed there.

In contrast to generators based on an azide charge, expensive filtering of the slag can be dispensed with, since the slag contains no toxic constituents. It consists mainly of carbonates and chlorides of potassium and sodium, along with very little nitrates/nitrites and zinc oxide. The discharge of such non-toxic constituents is therefore generally only limited by the limits set for the emission of dust.

The following examples are intended to explain the invention in more detail, but without limiting it.

The specified components for the gas charges according to the invention are homogenised for 30

minutes in the stated proportions by weight in plastic containers in an eccentric tumbling mixer. Tabletting of the mixtures to blanks with a diameter of about 6 mm is then effected. 3.5 g of the tabletted samples are caused to react using 0.2 g boron/potassium nitrate (25:75 parts by wt.) as an igniting mixture and an electrically heatable iron wire in a 25 ml stainless steel pressure bomb. The pressure-time curve of the reaction is recorded using a piezoelectric measuring device. Combustion gases which are composed mainly of H_2O, CO_2, N_2 and O_2 and meet the toxicological requirements set are formed in the exothermic reaction.

The gas charge mixtures described in the examples are investigated, for example in a measuring apparatus comprising a combustion chamber, gas flow diversion and filter chamber, using specific mechanical constructional conditions, to determine its combustion characteristics. The gaseous reaction products are collected and characterised in a 60 l volume vessel (main constituents: H_2O, CO_2, N_2 and O_2).

	Composition (wt. %)				
Example No.	1	2	3	4	5
5-aminotetrazole	33.1	33.1	34.0	33.1	34.2
sodium nitrate	52.3	52.3	61.5	52.3	64.8
potassium perchlorate	10.1	10.1	----	10.1	----
zinc oxide	4.0	3.0	1.0	----	----
zinc peroxide	---	1.0	3.0	4.0	----
graphite	0.5	0.5	0.5	0.5	1.0

Example	Heat of explosion (kJ/g)	Friction sensitivity (N)	Impact sensitivity (J)
1	3.61	> 360	10
2	3.69	> 360	10
3	3.70	> 360	10
4	3.82	> 360	7.5
5	3.82	> 360	10

Results of measurements in the ballistic pressure bomb

Example	Maximum pressure (bar)	Time difference[1] 40-60% p(max) (ms)	Cold gas[2] (l/g)	CO (ppm)
1	715	6.7	0.41	1800
2	707	5.9	0.38	1100
3	729	6.1	0.41	2000
4	660	6.5	0.40	1800
5	730	6.7	0.41	3300

[1] duration of the reaction at between 40 and 60% of the maximum pressure, in milliseconds

[2] measured after cooling to room temperature.

Example 1 describes the reaction of 5-aminotetrazole (5-ATZ) with a binary mixture of oxidants. The reaction gas composition shows a content of 1800 ppm CO in the reaction gases after combustion in a closed pressure bomb. In Example 2 the addition of only 1 % by wt. of zinc peroxide surprisingly leads to a marked reduction in the proportion of CO to 1100 ppm with otherwise unchanged test parameters. The changes in the composition of the mixtures in Examples 3 to 5 lead to poorer results.

	Composition (wt. %)			
Example No.	6 (=1)	7	8	9
5-aminotetrazole	33.1	25.4	16.6	10.7
sodium nitrate	52.3	52.7	52.7	52.7
potassium perchlorate	10.1	10.2	10.2	10.2
Zn $(5\text{-ATZ})_2$	----	11.2	----	----
Ca $(5\text{-ATZ})_2$	----	----	20.0	----
Mg $(5\text{-ATZ})_2$	----	----	----	25.9
zinc oxide	4.0	----	----	----
graphite	0.5	0.5	0.5	0.5

Example	Heat of explosion (kJ/g)	Friction sensitivity (N)	Impact sensitivity (J)
6 (=)1	3.61	> 360	10
7	3.64	> 360	10
8	3.46	> 360	15
9	2.74	> 360	20

Results of measurements in the ballistic pressure bomb (25 ml):

Example	Maximum pressure (bar)	Time difference[1] 40-60% p(max) (ms)	Cold gas[2] (l/g)	CO (ppm)
6 (=1)	715	6.7	0.41	1800
7	662	6.8	0.39	250
8	602	6.6	0.40	140
9	81	39.2	0.33	100

Results of measurements in the 60 l test canister:

Example	CO reduction[3] (%)	Maximum pressure[4] (bar)
6 (=1)	0	2.2
7	10	2.1
8	40	1.7
9	95	< 1.5

[1] duration of the reaction between 40 and 60% of the maximum pressure in milliseconds

[2] measured after cooling to room temperature

[3] based on the test canister results, Example 1 or 6

[4] mass of charge 40 g.

Examples 6 to 9 show that the addition of the Zn, Ca and Mg salts of 5-aminotetrazole ($Me(5\text{-}ATZ)_2$) has a favourable effect on the reaction gas composition. A marked reduction is found in the proportion of CO. The rate of reaction is also affected.

Example No.	Composition (wt. %) 10	11	12	13
5-aminotetrazole	33.0	31.6	30.8	28.9
guanidine nitrate	8.3	8.0	7.8	7.3
sodium nitrate	58.2	39.0	27.1	----
strontium nitrate	----	20.9	33.8	63.3
graphite	0.5	0.5	0.5	0.5

Example	Heat of explosion (kJ/g)	Friction sensitivity (N)	Impact sensitivity (J)	Mass of residue[3] (g)
10	4.06	> 360	20	1.5
11	3.90	> 360	15	1.2
12	3.61	> 360	20	1.0
13	3.41	> 360	15	0.8

Results of measurements in the ballistic pressure bomb (25 ml):

Example	Maximum pressure (bar)	Time difference[1] 40-60% p(max) (ms)	Cold gas[2] (l/g)
10	779	6.1	0.46
11	767	7.0	0.41
12	723	7.3	0.42
13	620	8.6	0.39

1) duration of reaction at between 40 and 60% of the maximum pressure, in milliseconds

2) measured after cooling to room temperature

3) mass of solids in the 60 l test canister after combustion of 30 g gas charge in the experimental generator.

Examples 10 to 13 differ in the proportion of sodium nitrate/strontium nitrate used as oxidant. With increasing proportions of strontium nitrate, the mass of the slag emerging into the canister decreases. This means that the filterability of the slag is improved by the addition of strontium nitrate - after the reaction - to the filter of the generator. At the

same time the proportion of CO in the reaction gas can be favourably influenced.